TRACKING IRON CATALYSTS IN HYDROTREATED BLIND CANYON COAL

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Introduction

In the past several years we have researched the dispersion of iron based catalysts within coal and coal macerals. This work has focussed not only upon the dispersion itself, but also upon the effect of the catalyst dispersion on the efficiency of the coal liquefaction process.

In experiments done with vitrinite and resinite macerals derived from Hiawatha (Utah) coal we found that an acetone soluble iron catalyst is more readily dispersed within the vitrinite than within the resinite maceral.[1] Using petrographic, IR spectroscopy and thermogravimetric analysis of the products, we determined that the vitrinite macerals had undergone a greater degree of depolymerization than the resinite maceral. In fact, the degree of aromaticity had increased in the resinite maceral indicating an overall loss of hydrogen during the hydrotreatment process. This retrograde process in the resinite maceral was attributed to the incomplete dispersion of the iron catalyst throughout this maceral.[1]

Further research with a suite of coals from the Argonne Premium Coal Sample Program indicated that the C, H, O elemental composition of the coal plays an important role in the catalyst dispersion and the efficiency of the liquefaction process.[2] It was

found that Wyodak, a low rank coal, gave a significantly greater yield of tetrahydrofuran (THF) solubles than does Pittsburgh #8, a higher rank coal. This result was attributed, in part, to the oxygen content of the coals. Wyodak coal has more oxygen, and this permits a greater degree of cross linking to occur during the hydrotreatment process. Cross linking preserves the pore structure of the coal thus facilitating the movement of the catalyst into the interior of the coal particle. In Pittsburgh #8, with a lower oxygen content than Wyodak coal, less cross linking occurs during hydrotreatment resulting in a poorer dispersion of the catalyst and a lower yield of THF solubles.[3]

In the past year we have been working with different forms of iron based coal liquefaction catalysts. The present paper covers some of our latest results that involve a comparison of catalyst efficiency and dispersion for various iron based catalysts with Blind Canyon (Utah) coal (DECS-17 from the Penn State Coal Sample Bank).

Experimental

The results reported in the present preprint were obtained using sealed glass tube reactors. Each reactor vessel contained 200 mg of catalyst impregnated DECS-17 coal and 400 mg of 9,10-dihydrophenanthrene which served as the hydrogen donor for the experiment. The catalyst loading for these experiments was 1 wt% by iron (and 1 wt% Mo or W in the case of the bimetallic catalyst systems). The sealed reaction vessels were then heated at 350°C for one hour. The THF solubles were obtained via soxhlet

extraction.

Catalysts were prepared in the following manner: If the catalyst was a dry, insoluble powder, the coal and catalyst were simply mixed together. Some coal samples were impregnated with catalysts derived from water soluble salts by an incipient wetness technique. The Mach 1 iron oxide catalyst was obtained from the Mach 1 Corporation (King of Prussia, PA). Presulfided Mach 1 was prepared in the following manner: 1 g of Mach 1 was placed in a tube oven. H_2S gas (1 atm) was allowed to saturate the sample, which was then heated to 400°C for two hours; the Mach 1 powder turned black. Upon exposure to air the catalyst underwent combustion and returned to a rust color.

The degree of dispersion of the catalyst systems was determined by making electron probe microanalysis (EPMA) micrographs of the THF insoluble fraction of the product. EPMA is a technique which allows one to map the dispersion of a given chemical element within a sample by the detection of characteristic X-rays.[4] The coal samples were mounted in Petropoxy 154 and polished to the required smoothness on a Syntron diamond paste polisher. Visual images were obtained using both secondary electron images (SEM) and back-scattered electron images (BSE). EPMA micrographs were obtained for iron and sulfur, and when necessary for molybdenum and tungsten.

The glass tube studies reported here will be repeated using a shaken, horizontal, tubing bomb reactor. These tubing bomb reactions will be done at 350°C for one hour and 2000 psig H_2. THF solubles yields and EPMA micrographs will be obtained.

Results

The present results are for the glass tube experiments. Data from the tubing bomb reactions will be presented at the Denver meeting.

EPMA micrographs for raw, hydrotreated DECS-17 coal show very little background iron and no molybdenum. The expected sulfur background is seen evenly dispersed throughout the particle. The images obtained for the iron/molybdenum bimetallic, soluble salt derived catalyst exhibit the following pattern: The iron has fully penetrated the coal particle and maps onto the sulfur; the molybdenum has also entered the coal particle. To some extent the molybdenum has collected in two void spaces within the particle (Figures 1a and 1b). The EPMA micrographs of the iron/thiotungstate impregnated sample tell a different story. In this case the iron generally remains outside the coal particle (Figure 2a). The sulfur and tungsten EPMA micrographs map onto each other very nicely, but neither sulfur nor tungsten has fully penetrated the coal particle. Instead, the thiotungstate remains near the exterior of the coal particle forming a halo (Figure 2b).

Two other samples were examined using EPMA. Both of these samples involved catalysts that are made of finely granulated iron oxide powders: Mach 1 and an Fe_2O_3/MoO_4 catalyst from the laboratory of Dr. Irving Wender (University of Pittsburgh). In the case of the presulfided Mach 1 catalyst the iron does not enter the coal particle. The iron and sulfur map onto each other indicating that some sulfur remains present even after the combustion process that

the catalyst underwent after presulfidation. The iron remains clumped together, a feature which was seen in samples treated with unsulfided Mach 1 (Figure 3). No molybdenum was added, and no molybdenum was found in the EPMA micrographs. According to EPMA micrographs (not shown), the catalyst provided by Irving Wender also did not enter the coal during hydrotreatment. The EPMA micrographs of the coal (not the catalyst) particles show typical native sulfur and iron backgrounds and no trace of molybdenum.

Due to the inherent uncertainties associated with the use of sealed glass tubes (i.e., loss of gaseous products and incomplete collection of the solid product), we do not report any THF solubles yields in this preprint. THF solubles yields will be reported at the Denver meeting for the reactions conducted in the tubing bomb reactors.

Conclusions

Water soluble salts are the most completely dispersed catalysts in the coal particles. In the case of the iron/molybdenum combination, the metallic species have fully penetrated the coal particle. Even though Mach 1 exists as a very fine particulate (average diameter 30 Å) it does not enter the coal particle. If the efficiency of the coal liquefaction process depends upon catalyst dispersion then soluble catalysts introduced by the incipient wetness technique have a significant advantage over insoluble, particulate based catalyst systems.

Acknowledgements

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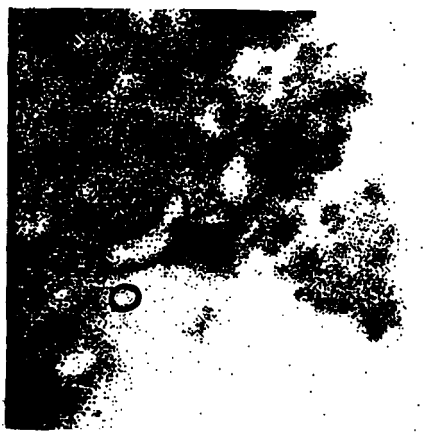

Figure 1a. This EPMA micrograph is 45μm by 45μm. The coal particle occupies the left and center of the image. Iron is well dispersed throughout this region. Note two void spaces circled in the figure.

Figure 1b. The EPMA micrograph is 45μm by 45μm and maps the Mo content of the coal particle. The coal particle occupies the left and center of the image. The Mo is well dispersed throughout the particle with two regions of greater concentration (circled) occurring in void spaces of the particle.

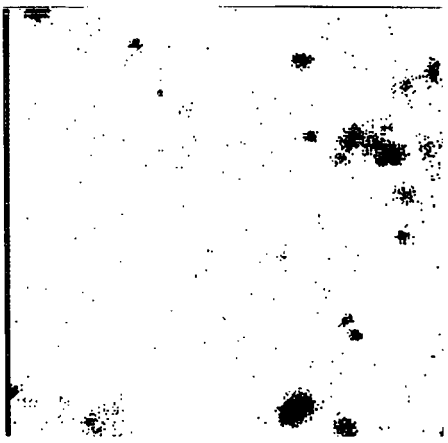

Figure 2a. The EPMA micrograph is 45μm by 45μm and represents the iron distribution in the coal particle. In this image the coal particle occupies the top and center. Only a small area has been penetrated by iron along the right side of the particle.

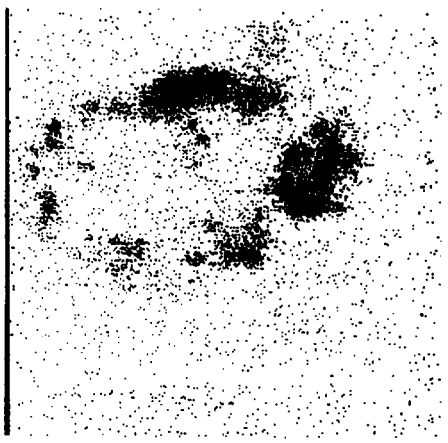

Figure 2b. The EPMA micrograph is 45μm by 45μm and represents the tungsten distribution within the coal particle. The tungsten has not fully penetrated the particle. Instead, it forms a halo at the edges of the coal particle.

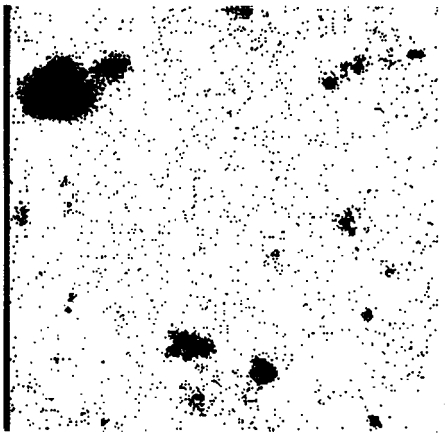

Figure 3. The EPMA micrograph is 45μm by 45μm and represents the iron distribution within the coal particle. In this image the coal particle occupies the center. The iron has not entered the particle and remains clumped outside the coal particle.